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(54) Ionically cross-linked low molecular weight ternary copolymer.

(57) An ionically cross-linked low molecular weight ternary copolymer which comprises reacting at least a part or the whole of acid groups in a low molecular weight ternary copolymer with a metallic cation selected from valences of 1 to 3, a content of ethylene being 80 - 99.5 mol% and a total content of acrylic or methacrylic acid and alkyl acrylate or methacrylate being 0.5 - 20 mol% in the above low molecular weight ternary copolymer, a ratio of composition between the acid and the ester being 10 - 90 to 90 - 10%, and a viscosity-average molecular weight of the low molecular weight ternary copolymer being within a range of 500 - 20,000.

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## SPECIFICATION

1. Title of the Invention

IONICALLY CROSS-LINKED LOW MOLECULAR WEIGHT TERNARY COPOLYMER

2. Background of the Invention(1) Field of the Invention

5 The present invention relates to a low molecular weight ternary copolymer cross-linked ionically with a novel metallic ion and the composition wherein such ionically cross-linked low molecular weight ternary copolymer is utilized.

More specifically, the present invention relates to an  
10 ionically cross-linked low molecular weight ternary copolymer prepared by reacting at least a part or the whole of acid groups in a low molecular weight ternary copolymer of ethylene-acrylic acid-alkyl acrylate or ethylene-methacrylic acid-alkyl methacrylate with a metallic cation selected from a valence of  
15 1, 2 and 3 as well as a composition obtained by incorporating said copolymer with a synthetic resin such as thermoplastic resin or the like and/or a fine inert material.

(2) Description of the Prior Art

A number of ethylene copolymers ionically cross-linked  
20 with metallic ion have heretofore been known. As an old example, Japanese Patent Publication No. 6810/1964 discloses an ionically cross-linked copolymer prepared by reacting a copolymer of ethylene- $\alpha$ ,  $\beta$ -ethylenically unsaturated carboxylic acid with a water-soluble ionic metal compound.

Furthermore Japanese Patent Publication No. 31556/1974 is characterized by saponification reaction of a copolymer prepared from ethylene and  $\alpha$ ,  $\beta$ -ethylenically unsaturated carboxylic ester by the use of a basic metallic compound in aliphatic 5 alcohols or an organic solvent containing aliphatic alcohols, and acid treatment of the saponified reaction product.

In both the above prior inventions, however, only ionic cross-linked products of high molecular weight are obtained.

With respect to ionic copolymers of low molecular weight, 10 metallic salts of binary copolymers have been known. For example, according to Japanese Patent Laid-open No. 128704/1982, low molecular weight copolymer salts obtained by neutralizing up to 100% a low molecular copolymer of copolymer acid comprised of ethylene and an  $\alpha$ ,  $\beta$ -ethylenically unsaturated carboxylic acid 15 and having a molecular weight of about 500 to about 15000 with cations of metals selected from Group IIA of the Periodic Table of Elements have been proposed.

It may be said, however, that this prior art directs to low molecular weight copolymer salts of binary copolymer acid 20 comprised of essentially ethylene and  $\alpha$ ,  $\beta$ -ethylenically unsaturated carboxylic acid.

The above described binary copolymer salts involve problems such as corrosion of apparatus and the like, besides it is difficult to produce copolymer acid having a desirable 25 molecular weight and acid value, because of high temperature and high pressure in the case where such copolymer acids have previously been produced. Thus, when it is intended that such

copolymer acids as described above are used as lubricants and dispersion aids for various polymers, melting point and softening point of these copolymer acids cannot be freely controlled so as to be adapted for the various polymers, so that  
5 there is a tendency of lacking wide adaptability.

### 3. Objects of the Invention

It is a first object of the present invention to provide a novel ionically cross-linked low molecular weight ternary copolymer having wide adaptability suitable for lubricants,  
10 dispersion aids, coupling agents, crystallization promoters, crystal nucleus agents, paints, adhesives, sealing materials, textile treatments and the like for varieties of polymer and inert material.

A second object of the present invention is to provide  
15 compositions comprised of various polymers and said ionically cross-linked low molecular weight ternary copolymer, and these compositions are those for improving workability, moldability and the like properties of varieties of polymer.

A third object of the present invention is to provide  
20 compositions comprised of various polymers, various fine inert materials and said ionically cross-linked low molecular weight ternary copolymer, and these compositions are applied for fine inert material as dispersion aids, coupling agents, crystallization promoters or the like and function to improve  
25 dispersibility of fillers, pigments and the like, or dimensional stability, mechanical strength and the like of molded articles.

#### 4. Detailed Description of the Invention

The present invention has been made as a result of concentrating inventors' energies on the above-mentioned problems.

5 In this connection, the present first invention provides...  
an ionically cross-linked low molecular weight ternary copolymer characterized by reacting at least a part or the whole of acid groups in a low molecular weight ternary copolymer with a metallic cation selected from valences of 1 to 3, a content of ethylene being 80 - 99.5 mol% and a total content of acrylic or methacrylic acid and alkyl acrylate or methacrylate being 0.5 - 20 mol% in said low molecular weight ternary copolymer, a ratio of composition between said acid and said ester being 10 - 90 to 90 - 10%, and a viscosity-average molecular weight of said low  
10 molecular weight ternary copolymer being within a range of 500 - 20,000.

The low molecular weight ternary copolymer used in the present invention may be directly produced in accordance with a common polymerizing process, but preferably a thermally degraded  
20 product which is produced by pyrolyzing commercially available ethylene-alkyl acrylate or methacrylate (hereinafter referred to simply as "(meth)acrylate") is utilized.

Namely, ethylene-acrylic or -methacrylic acid (hereinafter referred to simply as "-(meth)acrylic acid") -alkyl  
25 (meth)acrylate copolymer can be produced from a low molecular weight ternary copolymer which is said thermally degraded product in accordance with such a manner that, for example,

ethylene-alkyl (meth)acrylate copolymer having a comparatively high molecular weight is reacted at a temperature of 200 - 500°C and a pressure of 5 - 500 kg/cm<sup>2</sup> in the presence of water in inert atmosphere. The ethylene-alkyl (meth)acrylate copolymers referred in the present invention are such commercially available ethylene-alkyl (meth)acrylate copolymers of comparatively high molecular weight within such extent where these copolymers are easily produced by, for example, high-pressure copolymerizing process in which a free-radical catalyst is used and which is publicly known in the art, and a melt index of said ethylene-alkyl (meth)acrylate copolymer being about 300 g/10 min. or less, an alkyl acrylate content in the molecular chain being about 0.5 - 25 mol%, and preferably 2 - 15 mol%. While a manner for producing the inert atmosphere in the present invention is not specifically limited, such a manner that an inert gas such as nitrogen, carbon dioxide gas, argon, helium or the like is passed through the reaction system to completely exclude air therefrom is suitable, and among others use of nitrogen is preferable.

Furthermore the reaction temperature and pressure in case of embodying the present invention depend upon factors of properties of materials to be used, i.e., average molecular weight of ethylene-alkyl (meth)acrylate copolymer, content of alkyl acrylate, degree in degrading polymer, besides amount of extent water and the like, but usually such a reaction temperature, reaction pressure, and reaction time is within each

range of 200 - 500°C, 5 - 500 kg/cm<sup>2</sup>, and 1 - 10 hours, preferably 2 - 6 hours, respectively.

In the case where said reaction temperature is 200°C or less, degradation of copolymer is scarcely observed, whilst when the temperature exceeds 500°C, alkyl acrylate in the copolymer volatilizes, besides decarboxylating reaction and the like occur, so that pyrolysis becomes strong and this is undesirable.

Although a viscosity-average molecular weight of said low molecular weight ternary copolymer is different dependent upon its various applications, it is generally within a range of about 500 - 20,000, and preferably about 1,000 - 15,000.

Viscosity-average molecular weight referred in the present invention is determined by measuring intrinsic viscosity  $[\eta]$  at 135°C in decalin and calculating in accordance with the following equation:

$$[\eta] = KM^{\alpha}$$

$$(K = 14.3 \times 10^{-5} (\text{dl/g}), \alpha = 0.82)$$

Among the low molecular weight ternary copolymer thus produced, those having an ethylene content within a range of 80 - 99.5 mol%, and a (meth)acrylic acid and alkyl (meth)acrylate total content within a range of 0.5 - 20 mol% are utilized.

Because of cross-linking due to metal ion in the present invention, a ratio of moieties of (meth)acrylic acid and alkyl (meth)acrylate existing in the molecular chains of the low molecular weight copolymer produced is an important factor for deciding physical properties of the ionically cross-linked copolymers.

For example, it is necessary for adjusting the (meth)acrylic acid moiety existing in the molecular chains of a ethylene-(meth)acrylic acid-alkyl (meth)acrylate ternary copolymer in order to obtain a desirable acid value, so that amount of the remaining alkyl (meth)acrylate moiety changes. Moreover, when content of alkyl (meth)acrylate in a raw material of comparatively high molecular weight ethylene-alkyl (meth)acrylate is changed, it is possible that amount of (meth) acrylic acid moiety in the low molecular weight ternary copolymer produced is kept constant and amount of alkyl (meth) acrylate moiety is changed. In other words, when acid value is maintained at constant and amount of alkyl (meth)acrylate is changed, it is possible to vary melting point and softening point of low molecular weight copolymers, whereby these copolymers can be applied to varieties of use.

Namely, it is important in the present invention that a ratio of the (meth)acrylic acid moiety and alkyl (meth)acrylate moiety existing in its molecular chains is maintained within a range of 10 - 90%.

In the case where (meth)acrylic acid moiety is 10% or less, ionic cross-linking is insufficient in respect of metal ion, whilst when exceeded 90% or more, the resulting product becomes one being substantially binary copolymer and this is undesirable.

The alkyl (meth)acrylate in said ethylene-(meth)acrylic acid-alkyl (meth)acrylate copolymers involves preferably an



alkyl group having 1 - 4 carbon atoms such as methyl, ethyl, isopropyl, n-butyl, isobutyl, tertiary butyl or the like group.

Such metal ion to be added to said low molecular weight ternary copolymer in the present invention is preferably added in the form of aqueous solution of a metallic compound having a valence of 1 - 3 and which is selected from a first ion group consisting of (1)  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ , (2)  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Sb}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Fe}^{++}$ , (3)  $\text{Al}^{+++}$ ,  $\text{Fe}^{+++}$ , and the like as well as the mixture thereof, and among others, alkaline metal ion is particularly preferable. Furthermore such metallic compounds constituting a second ion group include, as so-called basic metallic compound, sodium hydroxide, magnesium hydroxide, potassium hydroxide, zinc hydroxide, calcium oxide, sodium methoxide, sodium ethoxide, magnesium oxide, nickel acetate, sodium carbonate, magnesium acetate, zinc acetate and the like, and aqueous solution of these metallic compounds may preferably be employed.

More preferable metallic cations are  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ , and  $\text{Zn}^{++}$  cations, and the low molecular weight ternary copolymers of the present invention are cross-linked therewith. Cation-containing materials are preferably hydroxides, oxides, oxydates, or acetate group.

According to the present invention, arbitrarily oligomerized cross-linked ternary copolymers may be produced by reacting ethylene-alkyl (meth)acrylate copolymer of a comparatively high molecular weight as its raw material in the presence of water and a metallic ion in inert atmosphere under

conditions at a temperature of 200 - 500°C and a pressure of 5 - 500 kg/cm<sup>2</sup>, and the most important factors in these reaction conditions are the presence of water and the temperature conditions. In this connection, the water in the present invention includes one in the form of liquid, steam, and the mixture thereof.

Dependent upon said temperature conditions and amount of water, it is possible to maintain molecular weight of said ethylene-alkyl (meth)acrylate copolymer at any low molecular weight, and at the same time an ionically cross-linked ethylene-alkyl (meth)acrylate-(meth)acrylic acid ternary copolymer in which arbitrary amount of alkyl (meth)acrylate remains can be produced.

The reaction between acid groups in the low molecular weight ternary copolymer and a metallic cation in the present invention is a neutralizing reaction, and at the same time or succeeding ionic cross-linkages are produced.

When this neutralized reaction product is compared with an unneutralized product, melt viscosity increases remarkably with increase in degree of neutralization. From this fact, it is found that there are ionic cross-linkages so that this is clearly distinguished from a mere salt. Metallic ion may be added in accordance with either a manner wherein such a metallic ion is added at the same time in decomposition reaction of said ethylene-alkyl (meth)acrylate copolymer, or a manner the produced low molecular weight ternary copolymer is post-

crosslinked with such a metallic cation. Method for post-crosslinking is as follows. A ternary copolymer is supplied together with a cation-containing material to a reaction vessel. Oxygen content in the reaction vessel is made minimum as much as possible, and volatile reaction products are removed during the reaction. Temperature in the reaction vessel is controlled while maintaining such temperature at melting point or more, and the reaction mixture is continuously agitated to react the same.

A part or the whole of (meth)acrylic acid in low molecular weight ternary copolymer may be reacted with said metallic cation, but preferable is to react 15% through 90% of the (meth)acrylic acid.

The copolymer thus cross-linked with the metallic cation is in solid state, so that the ionically cross-linked copolymer is more tough and more fragile than such copolymer which has not yet been cross-linked. The cross-linked product can be ground with a hardness of approximately the same with that of powder. When heated, ionic cross-linkages begin to break so that the viscosity of copolymer decreases. With the progress of cutting in ionic cross-linkages, characteristic features of the melt become close to those of the copolymer itself. In the present invention, the low molecular weight ternary copolymer has a low molecular weight and a low viscosity.

The melt is easy to flow and does not exhibit generally fabrication quality of typical thermoplastic resin.

A low molecular weight ternary copolymer ionically cross-linked with a metallic cation is useful as a lubricant or

dispersion aid for polymers. Such polymer lubricant has an acid value of 10 to 160 before the cross-linking of copolymer. Acid value is indicated by milligram number of potassium hydroxide required for neutralizing 1 gram of ternary copolymer.

5       The ionically cross-linked low molecular weight ternary copolymers according to the present invention have remarkable advantages as the undermentioned lubricants and dispersion aids, besides they are also applicable as coupling agents, crystallization promoters, crystal nucleus agents, paints, adhesives, sealing materials, textile treatments, greige goods, 10 modifiers for polymer, modifiers for printing ink, masking reagents for film and the like.

      The present second invention provides a composition comprising (A) 100 parts by weight of at least one polymer selected from the group consisting of thermoplastic resins, 15 thermosetting resins, rubber, and the mixture thereof, and (B) 0.1 - 15 parts by weight of an ionically cross-linked low molecular weight ternary copolymer prepared by reacting at least a part or the whole of acid groups in a low molecular weight ternary copolymer with a metallic cation selected from valences 20 of 1 to 3, a content of ethylene being 80 - 99.5 mol% and a total content of acrylic or methacrylic acid and alkyl acrylate or methacrylate being 0.5 - 20 mol% in said low molecular weight ternary copolymer, a ratio of composition between said acid and said ester being 10 - 90 to 90 - 10%, and a viscosity-average 25 molecular weight of said low molecular weight ternary copolymer being within a range of 500 - 20,000, and the presence of said

ionically cross-linked low molecular weight ternary copolymer exhibits remarkable advantages as a lubricant in the case of processing of said polymer.

Lubricant is added to a polymer in order to decrease molten sticking thereof, to improve flowability thereof, and to more easily process the polymer. Furthermore such lubricant is generally used for decreasing melt viscosity of a polymer at its processing temperature and/or decreasing such friction between the polymer and the metal surface of a processing machine.

10 Typical examples of polymerizing lubricant known in the art include paraffin wax; polyethylene wax; calcium stearate; esters, alcohols and acids of stearate; esters, acids and salts of montan base; stearates; amide wax and the like. Moreover it is known in the art to use an ionic copolymer additive in 15 varieties of polymer for improving characteristic features thereof. Such ionic copolymers disclosed in the art may be prepared from copolymers of  $\alpha$ -olefin and  $\alpha$ ,  $\beta$ -ethylenically unsaturated carboxylic acid. These copolymers, however, exhibit generally high molecular weight, and they can improve physical 20 properties such as impact resistance, but cannot improve polymer properties relating to the processing therefor.

On one hand, it is difficult to conclude that said low molecular weight binary copolymer salt (Japanese Patent Laid-open No. 128704/1982) involves sufficient applicability as 25 lubricant or dispersion aid for polymers, because said binary copolymer salt cannot freely control melting point and softening

point of the polymers in the case where the acid concentration (acid value) of said copolymer salt is constant.

The ionically cross-linked low molecular weight ternary copolymer according to the present invention has wider applicability than that of said binary copolymer, so that said ternary copolymer is utilized for varieties of lubricant.

Examples of said polymers include homopolymers such as low-, medium- and high-density polyethylene, polypropylene, polybutene-1, poly-4-methyl-pentene-1 or the like, copolymers of ethylene or propylene, as their major component, and the other  $\alpha$ -olefin such as ethylene-propylene copolymer, ethylene-butene-1 copolymer, ethylene-hexene-1 copolymer, propylene-ethylene copolymer or the like, besides polyolefin polymers such as ethylene-vinyl acetate copolymer or the like, polystyrene polymers, ethylene-vinyl acetate copolymer saponified products, polyvinyl alcohol polymers, polyamide polymers such as nylon 6, 66, 12 or the like, polyester polymers such as polyethylene terephthalate, polybutylene terephthalate or the like, thermoplastic resins such as polyvinyl chloride polymers, ABS polymer, polycarbonate polymers, polyphenylene oxide, polyphenylene sulfide, polyether sulfone, polyarylate, polyether ketone, polyether imide, polyimide, polyamide imide, petroleum resin, fluorine polymers or the like, thermosetting resins such as phenolic resins, epoxides, urethane resins, urea resin, melamine resin, unsaturated polyester resins, guanamine resin, diallyl phthalate resin, vinyl ester resin, furan resin or the

like, and synthetic or natural rubbers such as ethylene-propylene copolymer rubber, ethylene-propylene-diene copolymer rubber, isoprene rubber, butyl rubber, styrene-butadiene copolymer rubber, polybutadiene, styrene-acrylonitrile copolymer  
5 rubber, polyurethane rubber, chlorosulfonated polyethylene, fluorine rubber, silicone rubber, Thiokol or the like.

The composition according to the present invention may contain 0.1 - 15 parts, preferably 0.5 - 10 parts, and more preferably 1.0 - 8 parts by weight of said ionically cross-linked low molecular weight ternary copolymer per 100 parts by  
10 weight of such a polymer as described above.

Lubricating action of the ionically cross-linked low molecular weight ternary copolymer according to the present invention acts upon both the inner and outer surfaces of polymer  
15 to be processed. Said ionically cross-linked low molecular weight ternary copolymers exhibit excellent thermal stability and function on the above described varieties of polymer. For example, such a self-lubricating agent for use in polyolefins represented by low-density polyethylene, ethylene- $\alpha$ -olefin  
20 copolymer low-density polyethylene, high-density polyethylene and polypropylene as well as styrene polymer or the like relates to compatibility of the lubricant with polymer to be lubricated. In case of selecting lubricant, physical properties to be taken into consideration are its viscosity and hardness relating to  
25 molecular weight, whilst chemical compatibility is also important. Chemical compatibility is based on mutual action between chemical structure and component such as solubility or

the like between molten lubricant and polymer melt. When a lubricant is suitably in conformity with a polymer to be lubricated, the lubricant acts more favourably on the interior of the polymer.

5        In addition to solubility, melting point of lubricant, particularly internally acting lubricant is also important. When melting point of a lubricant is substantially the same with that of a polymer to be lubricated, the molten lubricant acts upon the interior of its polymer melt thereby decreasing torque  
10 at the time of processing. On one hand, when melting point of a lubricant is considerably lower than that of a polymer to be lubricated, such lubricant melts before the polymer softens completely. This results in excessive lubrication of the polymer by means of the lubricant. In extruder, such excessive  
15 lubrication occurs in feed and transfer sections thereof. On the other hand, when melting point of a lubricant is too high, a polymer melts first so that the lubricant exhibits excessive lubrication, and its torque decreases until both of them melt. In this case, although torque decreases, processing is not  
20 observed so that slipping state appears. Accordingly, the closer temperatures are the better with respect to softening points or melting points of both lubricant and polymer. In this respect, the low molecular weight ternary copolymers according to the present invention have an advantage of being capable of  
25 freely controlling their melting point and softening point.

Said lubricants are useful for method of processing polymers in various processing operations such as molding,



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extrusion and the like as well as mixing operations including roll milling, extrusion mixing, and internal mixing by means of Banbury mixer or the like.

A polymer to be processed is preferably pre-blended with the lubricant according to the present invention. Such pre-blending is a mere physical blending of the pellet polymer with the powdery or pellet-form lubricant. This blend is supplied to a processing equipment including molding equipment, extruder, mill, mixing extruder, or internal mixer. Polymer is separately supplied from lubricant to a processing equipment in mutual manner and dependent upon the processing equipment used.

Polymer is processed by means of assistance of lubricant. The lubricants according to the present invention may be used for processing a polymer at a temperature of from melting point of the polymer to about 400°C.

Furthermore Japanese Patent Publication Nos. 26225/1970 and 26226/1970 disclose a composition consisting of polyester such as polyethylene terephthalate or the like, ethylene, and an ionic copolymer of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid and wherein said ionic copolymer increases rate of crystallization and improves form stability of molded articles. However, the ionically cross-linked low molecular weight ternary copolymers according to the present invention elevate much more the above described advantages, and they function also as crystallization promotor or nucleating agent.

The present third invention provides a composition comprising:

(A) 100 parts by weight of at least one polymer selected from the group consisting of thermoplastic resins, thermosetting resins, rubber, and the mixture thereof;

(B) 0.1 - 150 parts by weight of a fine inert material; ...  
5 and the ionically cross-linked low molecular weight ternary copolymer according to the present invention, i.e.,

(C) 0.1 - 20 parts by weight of an ionically cross-linked low molecular weight ternary copolymer prepared by reacting at least a part or the whole of acid groups in a low  
10 molecular weight ternary copolymer with a metallic cation selected from valences of 1 to 3, a content of ethylene being 80 - 99.5 mol% and a total content of acrylic or methacrylic acid and alkyl acrylate or methacrylate being 0.5 - 20 mol% in said low molecular weight ternary copolymer, a ratio of composition  
15 between said acid and said ester being 10 - 90 to 90 - 10%, and a viscosity-average molecular weight of said low molecular weight ternary copolymer being within a range of 500 - 20,000, and the presence of said ionically cross-linked low molecular weight ternary copolymer exhibits remarkable advantages in the  
20 case where said fine inert material is dispersed into said polymer, so that said ionically cross-linked low molecular weight ternary copolymer is utilized as a dispersion aid.

Moreover said ionically cross-linked low molecular weight ternary copolymer may be used as a coupling agent and possesses  
25 also such function of suitably activating the surface of the fine inert material.

Heretofore, a typical example of the dispersion aid as described above includes low molecular weight polyethylene homopolymer.

Low molecular weight polyethylene homopolymer has been partially utilized as compatible dispersion aid for polymers, but it cannot be used for nylon, polystyrene, polycarbonate, and polyester as dispersion aid, because of incompatibility thereof.

In this connection, the ionically cross-linked low molecular weight ternary copolymers according to the present invention involve epoch-making advantage as dispersion aid.

More specifically, the dispersion aids according to the present invention are useful for dispersing a fine inert material into polymer. With respect to the object of the present invention, the inert materials to be used are those which are not molten at the melting point of a polymer into which such fine inert materials are dispersed. In general, an average diameter of a material to be dispersed is 100 microns or less, and a common diameter thereof is 50 micron or less.

Category of materials which may be dispersed by means of the dispersion aids according to the present invention involves inorganic, organic, natural and synthetic pigments; lake dyestuffs; insoluble dyestuffs; fillers; flame-retardants; anti-oxidants; stabilizers; and their simulants.

These typical materials include titanium dioxide, zinc oxide, calcium carbonate, barytes, silica and china clay; white lead; carbon black; red lead; lead chrome pigment; Venetian Red; Persian Blue; chrome oxides; chrome green; copper blue; and

cobalt blue. Typical lake dyestuffs include alumina dyed with a solution of natural organic colorants; and coal tar colorants deposited from solutions of various coal tar dyestuffs by means of metal salts, tannin or other suitable reagents.

5           Typically, fillers may be selected from varieties of mineral, metal, metal oxide, siliceous earth, and metal salt. An example of these fillers includes glass fiber, alumina, feldspar, asbestos, talc, calcium carbonate, clay, carbon black, quartz, novaculite and, as the other forms, silica, kaolinite, 10 bentonite, garnet, mica, sapo-nite, beidellite or the like. The above described fillers are for the purpose of a mere explanation, but the fillers used in the present invention are not limited thereto.

          In the present invention, 0.1 to 150 parts, preferably 15 0.1 to 70 parts by weight of fine inert material may be dispersed into 100 parts by weight of polymer. A lower concentration 0.1 to 1 part by weight of such fine inert material per 100 parts by weight of polymer is applicable for direct blending of a low concentration material such as a 20 colorant or the like. A higher concentration material of about 10 parts by weight or more is directly introduced into polymer. A high concentration material of about 10 to 70 parts by weight per 100 parts by weight of polymer is utilized for masterbatch of a colorant concentrate or the like in order that such high 25 concentration material is introduced into much more the same or different polymer.

The dispersion aids according to the present invention may be used for varieties of polymer, and examples thereof include said thermoplastic resins, thermosetting resins, rubbers, and the mixtures thereof.

5       The dispersion aid of the present invention may be 0.1 - 20 parts, preferably 0.1 - 10 parts by weight with respect to 100 parts by weight of polymer.

The dispersion aids according to the present invention can be prepared by means of any publicly known process in the  
10 art for producing ionically cross-linked low molecular weight ternary copolymers.

The dispersion aids of the present invention exhibit excellent thermal stability, and they may be used for varieties of polymer. The dispersion aids of the invention do not  
15 volatilize or discolor during processing. In definition, "compatibility" may be concluded as such ability to keep a situation where two or more of components are blended with each other so that a certain component is homogeneously dispersed in the other components. Physical compatibility depends upon  
20 processing conditions as well as physical properties of a dispersion aid and a polymer. Compatibility of a dispersion aid with a polymer relates to physical properties of the dispersion aid by which viscosity and hardness of said ionically cross-linked low molecular weight ternary copolymer concerning the  
25 molecular weight are influenced.

Furthermore chemical compatibility is also important, and which is based on mutual action between components such as

chemical structure, solubility between molten copolymer and polymer melt or the like. Such dispersion aid having the more favorable compatibility with a polymer exhibits the more homogeneous dispersibility.

5 In addition to compatibility, melting point of the dispersion aids is also an important factor. In the maximum dispersion, melting point of such dispersion aid should be kept at low temperature as much as possible accompanied with no excessive lubrication. Generally, such dispersion aid melts  
10 before a polymer into which a fine material is dispersed melts. With flow of the material through resin, the dispersion aid wets the material and draws the same along said material.

The present invention includes a method for treating polymer in order to finally maintain the maximum dispersion of  
15 inert material. At first, a polymer, a dispersion aid, and a material to be dispersed are firmly blended with each other. The dispersion aid and polymer are in powdery form, pellet- or tip-shape, whilst the material to be dispersed is preferably powdery. Then, the blend is fed to a means which melts the  
20 blend at a higher temperature of both the melting points of the polymer and dispersion aid and compounds the blend. Otherwise the dispersion aid may be firmly admixed with the material to be dispersed. The admixture of the dispersion aid and the material to be dispersed is then mixed with the polymer, and the final  
25 mixture is molten and blended. The dispersion aid and the material to be dispersed thus molten and blended are then formed into pellet or other suitable shape, and they are firmly either

admixed or molten and blended with the polymer. Such melting and blending means may include molding equipment, extruder, mill, mixing extruder, internal mixer and the like.

The dispersion aid according to the present invention may  
5 be incorporated in a polymer at a temperature of the melting point of the polymer or more through about 400°C. Then, the polymer product thus formed and blended is collected.

Some examples will be described hereinbelow for the sake  
of explaining the true nature of the present invention as well  
10 as a method for embodying the invention, but it should not be considered that the present invention is limited to such detailed description.

The present invention relates to a novel, ionically cross-linked low molecular weight ternary copolymer, and which  
15 can be easily and arbitrarily oligomerized from a commercially available high molecular weight binary copolymer. Accordingly, properties required for lubricant or dispersion aid can be freely controlled in the present ionically cross-linked low molecular weight ternary copolymers, so that they involve wide  
20 applicability.

Furthermore the ionically cross-linked low molecular weight ternary copolymers according to the present invention possess not only remarkable advantages as lubricant and dispersion aid, but also functions of crystallization promotor,  
25 nucleating agent, and coupling agent.

Moreover the ionically cross-linked low molecular weight ternary copolymers according to the present invention are

utilized as modifiers or the like for said paints, adhesives, textile treatments, sealing materials, and polymers.

The invention will be described in more detail hereinbelow in conjunction with examples.

5 Reference Examples 1 - 4

A pressure vessel of 3.8 l internal volume and equipped with a magnetic stirrer was charged with 2 kg of ethylene-ethyl acrylate copolymer (ethyl acrylate content being 4.4 mol%, melt index being 9 g/10 min.) together with 1 kg of water. Nitrogen  
10 gas was bubbled from the bottom of said vessel for 1 hour to completely exclude oxygen dissolved in the water. Then, pressurizing ( $50 \text{ kg/cm}^2$ ) and releasing ( $1 \text{ kg/cm}^2$ ) operations of nitrogen gas were repeated five times with respect to air inside said pressure vessel, and when oxygen concentration in the  
15 system was measured (Brady method), it was 1 ppm or less. The vessel was then heated, whereby thermal degradation was effected in nitrogen atmosphere at  $350^\circ\text{C}$  under  $100 \text{ kg/cm}^2$  for 4 hours.

It was found from infrared absorption curve that the product was ethylene-acrylic acid-ethyl acrylate ternary  
20 copolymer, the composition of which involved 95.6 mol% ethylene ( $1460 \text{ cm}^{-1}$ ), 3.0 mol% acrylic acid ( $1700 \text{ cm}^{-1}$ ), and 1.4 mol% ethyl acrylate ( $1730 \text{ cm}^{-1}$ ), and a viscosity-average molecular weight of which was 5,000.

Furthermore the raw material ethylene-ethyl acrylate  
25 copolymer in Reference Example 1 was pyrolytically decomposed at each temperature of  $340^\circ\text{C}$  and  $330^\circ\text{C}$  to prepare a product having a molecular weight of 7,000 (Reference Example 2) and a product



- 24 -

having a molecular weight of 10,000 (Reference Example 3), respectively, and analyzed results of the composition or the like thereof are indicated in Table 1.

Moreover, as Reference Example 4, the raw material ethylene-ethyl acrylate copolymer (hereinafter referred to simply as "EEA") in Reference Example 1 was replaced by one having an ethyl acrylate content of 2.0 mol% and a melt index of 5.0 g/10 min., and degraded thermally as in the case of Reference Example 1. The results thereof are indicated in Table 1.

#### Examples 1 - 8

A pressure vessel of 3.8 l internal volume and equipped with a magnetic stirrer was charged with 2 kg of ethylene-ethyl acrylate copolymer (ethyl acrylate content being 4.4 mol%, melt index being 9 g/10 min.) together with 1 kg of water. Nitrogen gas was bubbled from the bottom of said vessel for 1 hour to completely exclude oxygen dissolved in the water. Then, pressurizing ( $50 \text{ kg/cm}^2$ ) and releasing ( $1 \text{ kg/cm}^2$ ) operations of nitrogen gas were repeated five times with respect to air inside said pressure vessel, and when oxygen concentration in the system was measured (Brady method), it was 1 ppm or less. The vessel was then heated, whereby the raw material was reacted under the same conditions with those of Reference Example 1, i.e., in nitrogen atmosphere at  $350^\circ\text{C}$  under  $100 \text{ kg/cm}^2$  for 4 hours. Thereafter, the reaction product was cooled to  $200^\circ\text{C}$ , and an aqueous solution prepared by dissolving 30 g of sodium hydroxide in 100 cc of water was poured into the reaction

product while succeedingly controlling the same at 200°C, the resulting mixture was reacted at 200°C under 50 kg/cm<sup>2</sup> for 1 hour while agitating it, and then cooled by standing in air. It was found from infrared absorption curve that the product was  
5 ethylene-acrylic acid-ethyl acrylate ternary copolymer cross-linked with Na<sup>+</sup>, the composition of which involved 95.6 mol% ethylene (1460 cm<sup>-1</sup>) and 1.4 mol% ethyl acrylate (1730 cm<sup>-1</sup>), and absorption displacement of carboxyl group based on acrylic acid (1700 cm<sup>-1</sup>) cross-linked with Na ion and ionic crosslinkage  
10 was observed at 1570 cm<sup>-1</sup> in 40% theoretical neutralization amount (1 mol of Na<sup>+</sup> ion was equivalent to 1 mol of acrylic acid).

In Example 2, amount of sodium hydroxide to be poured was increased to 70 g, and a cross-linked product having 90%  
15 theoretical neutralization percentage was produced in accordance with a similar manner to that of Example 1.

In Examples 3 - 6, thermal degradation was effected under similar conditions to those of Reference Examples 2 - 3, whilst a prescribed amount of Na ion was reacted by a similar manner to  
20 that of Example 1. The results thereof are shown in Table 1.

In Examples 7 - 8, thermal degradation was effected under similar conditions to those of Reference Example 4, whilst reaction was conducted by a similar manner to that of Example 1. The results thereof are shown in Table 1.

25 As indicated by melt viscosity in Table 1, the higher melt viscosity is derived from the higher molecular weight. With increase in amount of a metallic cation to be added, ionic

crosslinkage increases and the viscosity increases also. More specifically, with the progress of neutralization from 0 to 40% in Reference Examples 1 - 4, substantial increase in viscosity is observed, and further with the progress of neutralization from 40% to 80 through 90%, much more increase in viscosity is observed. (In this case, viscosity was measured by means of rotational viscometer (B-type viscometer).)

Table 1

## Ternary Copolymer

	<u>ET</u>	<u>AA</u>	<u>EA</u>	<u>M.W.</u>	<u>M.C.M.(g)</u>	<u>T.N.A.(%)</u>	<u>Vis.cps</u>
Ex.1	95.6	3.0	1.4	5,000	NaOH 30	40	1,780
2	95.6	3.0	1.4	5,000	" 70	90	30,300
3	95.6	2.5	1.9	7,000	" 26	40	5,800
4	95.6	2.5	1.9	7,000	" 58	90	50,200
5	95.6	2.0	2.4	10,000	" 21	40	48,200
6	95.6	2.0	2.4	10,000	" 46	90	C.N.M.
7	98.0	1.5	0.5	5,000	" 15	40	900
8	98.0	1.5	0.5	5,000	" 35	90	15,000
Re.Ex.1	95.6	3.0	1.4	5,000	-	0	510
2	95.6	2.5	1.9	7,000	-	0	2,100
3	95.6	2.0	2.4	10,000	-	0	10,200
4	98.0	1.5	0.5	5,000	-	0	490

Abbreviation of terms in Table:

ET = ethylene, AA = acrylic acid, EA = ethyl acrylate,  
M.W. = molecular weight, M.C.M. = metallic cation material,  
T.N.A. = theoretical neutralization amount, Vis. = viscosity,  
C.N.M = could not measured.

Reference Examples 5 - 6

As raw material EEA, EEA having 4.5 mol% ethyl acrylate content and 3.0 g/10 min. melt index and another EEA having 12.0 mol% ethyl acrylate content and 4.0 g/10 min. melt index were used, and thermally degraded products having each molecular weight of 7,000 and 8,800 were obtained under similar conditions to those of Reference Example 1 at each temperature of 340°C and 335°C. The analyzed composition is as shown in Table 2.

Examples 9 - 11

10        Examples 9 - 11 were conducted by cross-linking the ternary copolymers in said Reference Examples 5 - 6 with magnesium hydroxide. More specifically, 40 to 80% of carboxyl groups in the low molecular weight ternary copolymers were neutralized with use of theoretical amount of magnesium  
15 hydroxide (1 mol of  $Mg^{++}$  ion was equivalent to 2 mol of acrylic acid) to produce ternary copolymers cross-linked with magnesium cation. Reaction was effected by utilizing a pressurizing type kneader in laboratory. More specifically, about 300 g of the low molecular weight ternary copolymer shown in Comparative  
20 Example in Table 2 was placed in the pressurizing type kneader having about 3 l internal volume, and pressurizing ( $5 \text{ kg/cm}^2$ ) and releasing ( $1 \text{ kg/cm}^2$ ) operations of nitrogen gas were repeated ten times with respect to air inside said pressurizing type kneader to remove oxygen in the system. Then, a  
25 temperature of the contents in the kneader was raised to the reaction temperature of 170°C by means of electrical heating. The temperature was controlled at 170°C, and the reaction was

continued until either the reaction is completed, or no volatile matter is produced from reacting mass in the reaction vessel. A prescribed amount of magnesium hydroxide was gradually added to react the contents in the vessel while suppressing bubbling due to production of volatile matter.

Absorption displacement of carboxyl group based on ionic crosslinkage of Mg ion was observed at  $1620\text{ cm}^{-1}$ .

Although melt viscosity of a product cross-linked neutralizingly was tried to measure by means of a rotational viscometer (B-type viscometer), there was a sample which could not be measured. Accordingly, melt index was measured at  $190^{\circ}\text{C}$  (JIS K6760).

When examined Tables 1 and 2, it is found that with increase of acrylic acid in samples, amount of metallic cation required for neutralization of the same percentage increases. When compared sodium hydroxide with magnesium hydroxide in respect of metallic cation material, magnesium hydroxide produces divalent metallic cation. This provides two positions with respect to formation of ionic crosslinkage. Accordingly, number of moles for magnesium ion was made half that of sodium ion in order to attain substantially the same degree of neutralization.

It is expected that with increase in amount of metallic cation to be added, ionic crosslinkage increases and viscosity increases also, and this expectation has been just indicated in Tables 1 and 2. It is observed that with progress of neutralization from 0% in Reference Examples 1 - 6 to 40% in

Examples, substantial increase in viscosity (decrease in melt index) appears, and further with the progress of such increase from 40 to 80 through 90%, viscosity increases (decrease in melt index) further.

5        In addition, when composition of ethyl acrylate in the low molecular weight ternary copolymer is changed as shown in Example 11 and Comparative Example 16, it is possible to change both melting points of said copolymer and its metallically cross-linked product (DSC method). In the present Examples, 10 since such high molecular weight ethylene-ethyl acrylate copolymer raw material of high content ethyl acrylate is selected, a prescribed amount of acrylic acid is produced by means of thermal degradation, so that a metallically cross-linked ternary copolymer having low melting point is obtained. 15 This means that even in a copolymer involving composition of a given amount of acrylic acid (acid value), when amount of alkyl (meth)acrylate is changed, it is possible to change melting point of the copolymer and that said ternary copolymer is more advantageous than binary copolymer, when used as lubricant, 20 dispersion aid and the like.

Table 2

Ternary Copolymer mol%

	ET	AA	EA	M.W.	M.C.M.	T.N.A.	M.I. at	M.P.	
					<u>(g)</u>	<u>(%)</u>	190°C	<u>(°C)</u>	:
							<u>(°C)</u>		:
Ex. 9	95.6	2.4	2.0	7,000	Mg(OH) <sub>2</sub> 2.7	40	2,400	105	:
10	95.6	2.4	2.0	7,000	Mg(OH) <sub>2</sub> 5.4	80	560	102	:
11	88.4	3.4	8.2	8,800	Mg(OH) <sub>2</sub> 7.6	80	50	85	:
Re.Ex. 5	95.6	2.4	2.0	7,000	-	0	>10,000	107	:
6	88.4	3.4	8.2	8,800	-	0	3,100	87	:

Abbreviation of terms in Table:

M.I. = melt index, M.P. = melting point.



Reference Examples 7 - 10

(Production of Each Raw Material Alkyl (Meth)acrylate)

In the present Examples, each binary copolymer of a comparatively high molecular weight was prepared. In each  
5 Example, contents of a metallic autoclave type reactor having 3.8  $\text{m}^3$  internal volume and equipped with a stirrer were replaced sufficiently by nitrogen and ethylene. Then, the reactor was charged with a prescribed amount of ethylene, n-hexane of chain transfer agent, and a copolymer, and further di-tert-butyl  
10 peroxide of polymerizing initiator was poured, thereafter the mixture was polymerized at a polymerizing temperature of  $170^{\circ}\text{C}$  under the polymerizing conditions indicated in Table 3 for a polymerizing time of 1 hour.

As the copolymers, methyl acrylate, t-butyl acrylate,  
15 ethyl methacrylate, and i-propyl methacrylate were used, and a copolymer in the respective polymers produced was confirmed by infrared absorption analytical method and determined. The results thereof are indicated in Table 3.

These polymers were thermally degraded in accordance with  
20 a similar manner to that of Reference Example 1, and the results thereof are indicated in Table 4.

Table 3

Peroxide								
	ET	CP.	Press.	Temp.	di-T-BP	Yield	M.I.	CP.cot.
	(g)	(g)	(kg/cm <sup>2</sup> )	(°C)	(mmol)	(g)	(g/10m.)	(mol%)
Re.Ex. 7	1,700	MA60	1,600	170	0.05	320	2.1	4.2
" 8	1,700	t-BA100	1,600	170	0.05	380	9.4	5.6
" 9	1,700	EM90	1,600	170	0.05	340	6.7	5.3
" 10	1,700	i-PM60	1,600	170	0.05	360	8.7	2.1

Abbreviation of terms in Table:

CP. = copolymer, Press. = pressure, Temp. = temperature, di-t-BP = di-t-butyl peroxide, CP.cot. = copolymer content, MA = methyl acrylate, t-BA = t-butyl acrylate, EM = ethyl methacrylate, i-PM = i-propyl methacrylate.

Examples 12 - 19

In the present Examples 12 - 19, each degraded ternary copolymer obtained from the respective binary copolymers which had been prepared in Reference Examples 7 - 10 through thermal degradation as well as the low molecular weight ternary copolymers cross-linked with metallic cation were produced. Thermal degrading method was conducted in accordance with a similar manner to that of Examples 1 - 8, so that the resulting low molecular weight ternary copolymers were indicated as Reference Examples 7 - 10. Examples 12 - 19 were conducted in order that the low molecular weight ternary copolymers shown in Reference Examples 7 - 10 were cross-linked with sodium hydroxide and magnesium hydroxide. A cross-linking method was such that each copolymer was reacted by employing the pressurizing type kneader shown in Examples 9 - 11, and the cross-linked low molecular weight ternary copolymer was confirmed by means of infrared absorption analytical method and rotational viscometer. The results thereof are shown in Table 4.

Table 4

## Ternary Copolymer

	ET	Ac.	Est.	M.W.	M.C.M. (g)	T.N.A. (%)	Vis. at 200°C cps
Ex. 12	96.0	AA3.0	MA1.0	3,000	NaOH3.6	30	1,200
13	96.0	AA3.0	MA1.0	3,000	NaOH7.2	60	3,900
14	94.6	AA4.0	t-BA1.4	9,500	NaOH4.7	30	27,000
15	94.6	AA4.0	t-BA1.4	9,500	NaOH9.4	60	50,800
16	95.0	MAc1.9	EM3.1	4,500	NaOH2.2	30	1,300
17	95.0	MAc1.1	EM3.1	4,500	NaOH4.4	60	2,700
18	98.0	MAc1.5	i-PM0.5	8,000	Mg(OH) <sub>2</sub> 2.5	30	4,700
19	98.0	MAc1.5	i-PM0.5	8,000	Mg(OH) <sub>2</sub> 5.0	60	9,300
Re.Ex. 7	96.0	AA3.0	MA1.0	3,000	-	0	190
8	94.6	AA4.0	t-BA1.4	9,500	-	0	9,400
9	95.0	MAc1.9	EM3.1	4,500	-	0	430
10	98.0	MAc1.5	i-PM0.5	8,000	-	0	2,600

Abbreviation of terms in Table:

Ac. = acid, Est. = ester, MAc = methacrylic acid.

Examples 20 - 22 and Comparative Examples 1 - 2

In the following Examples 20 - 22 and Comparative Examples 1 - 2, ionically cross-linked low molecular weight ternary copolymers obtained by reaction of ethylene-acrylic acid-ethyl acrylate copolymer and sodium hydroxide were shown as lubricant for ethylene- $\alpha$ -olefin copolymer (straight chain low-density polyethylene). The reaction was effected in accordance with a similar manner to that of Examples 1 - 8. Lubricant A is one prepared by neutralizing 60% a copolymer having a viscosity-average molecular weight of 3,100 and a composition of 94.2 mol% ethylene, 4.0 mol% acrylic acid, and 1.8 mol% of ethyl acrylate with sodium hydroxide in accordance with said manner. On one hand, Lubricant B is one prepared by neutralizing 60% a ternary copolymer having a viscosity-average molecular weight of 11,000 and a composition of 94.2 mol% ethylene, 0.6 mol% acrylic acid, and 5.2 mol% of ethyl acrylate with sodium hydroxide similarly to that described above. Extruded form used in Examples 10 - 12 has 50 m/m screw diameter, and die has 1 m/m slit width. Each composition was sufficiently dryblended, and then once extruded and molten to be shaped into pellet form in order to complete homogeneous blending. Thereafter properties of the lubricant were tested with the use of 50 m/m extruder.

As the straight chain low-density polyethylene (LLDPE), Nisseki Linirex AF3310 (2.0 melt index, and 0.922 density) manufactured by Nippon Petrochemicals Co., Ltd. was used. On one hand, Nisseki Rexlon F312 (2.0 melt index, and 0.922 density) manufactured by Nippon Petrochemicals Co., Ltd. was

used as the low density polyethylene. In Examples 20 - 22, such result was observed that lower number of revolutions in screw than that of the case where no lubricant was used in Comparative Example 1 brought in substantially the same amount of discharge.

5 Besides, extreme end pressure of the extruder was also suppressed at low value in the present Examples, so that advantageous effects of the lubricant were apparent. Likewise, extreme end pressure of the extruder was also suppressed at low value in case of 20% LDPE blend composition, and improvement of  
10 working characteristics was observed. The results thereof are shown in Table 5.

Table 5

	<u>R.O.C. (wt%)</u>	<u>N.R. (rpm)</u>	<u>E.C. (Å)</u>	<u>H.P. (kg/cm<sup>2</sup>)</u>	<u>A.D. (g/m.)</u>
Ex. 20	LLDPE+LT.A 95 5	53	45	275	334
" 21	LLDPE+LT.B 95 5	53	45	285	331
C.Ex. 1	LLDPE 100	57	46	310	333
Ex. 22	LLDPE+LDPE+LT.A 75 20 5	53	45	260	336
C.Ex. 2	LLDPE+LDPE 80 20	54	45	290	329

Abbreviation of terms in Table:

R.O.C. = ratio of composition, N.R. = number of revolutions, E.C. = electric current, H.P. = head pressure, A.D. = amount of discharge, LT. = lubricant, C.Ex. = comparative example.

Examples 23 - 24 and Comparative Example 3

The present Examples demonstrate specific examples of ionically cross-linked ternary copolymers which were used as dispersion aids. A copolymer used as dispersion aid was an  
5 ionically cross-linked ternary copolymer having a viscosity-average molecular weight of 5,100 and a composition of 93.0 mol% ethylene, 4.2 mol% acrylic acid, and 2.8 mol% of ethyl acrylate, and 60% of acrylic acid of which were neutralized with magnesium hydroxide. As crystalline polypropylene, Nisseki Polypro J150G  
10 having 8 g/10 min. melt flow index and manufactured by Nippon Petrochemicals Co., Ltd. was used. As mica, Suzolite mica having 90  $\mu$ m weight-average flake diameter, 50 average aspect ratio, and 0.24 g/cc bulk specific gravity was used. As modified polypropylene, acrylic acid graft polypropylene having  
15 20 g/10 min. melt flow index and 6 wt% acrylic acid content was employed.

Experiment was conducted by such that the crystalline polypropylene, the modified polypropylene, the mica, and said ionically cross-linked low molecular weight ternary copolymer,  
20 as a dispersion aid, were introduced into a Henschel mixer, admixed at a rate of 720 rpm for 3 minutes, and the resulting admixture was formed into ASTM type dumbbell by means of an injection molding machine, thereafter tensile strength at yield point and other physical properties were measured by utilizing  
25 said dumbbell. In Comparative Example 3, materials were processed and measured in accordance with the same manner with



that of Examples 23 - 24 without adding any lubricant, and the results thereof are indicated in Table 6.

As is apparent from experimental Examples shown in Table 6, it was observed that polypropylene compositions mechanical properties of which had been improved were produced in the case where the low molecular weight ternary copolymer cross-linked with magnesium ion was used as a dispersion aid.

Table 6

<u>Composition</u>		<u>Ex. 23</u>	<u>Ex. 24</u>	<u>Comp. Ex. 3</u>
Polypropylene (55Crystalline + 5Modified)	wt%	60	60	60
Mica	"	39.7	38	40
I.C.L.MW.T.CP	"	0.3	2	
<u>Physical Properties</u>				
Tensile Strength at Yield Point	kg/cm <sup>2</sup>	360	380	260
Breaking Extension	%	10	15	10
Bending Strength	kg/cm <sup>2</sup>	610	680	470
Bending Modulus	"	62,000	65,000	58,000
Heat Distortion Temperature	°C	150	152	137

Abbreviation of term in Table:

I.C.L.MW.T.CP. = ionically cross-linked low molecular weight ternary copolymer.

CLAIMS

1. An ionically cross-linked low molecular weight ternary copolymer which comprises reacting at least a part or the whole of acid groups in a low molecular weight ternary  
5 copolymer with a metallic cation selected from valences of 1 to 3, a content of ethylene being 80 - 99.5 mol% and a total content of acrylic or methacrylic acid and alkyl acrylate or methacrylate being 0.5 - 20 mol% in said low molecular weight  
10 ternary copolymer, a ratio of composition between said acid and said ester being 10 - 90 to 90 - 10%, and a viscosity-average molecular weight of said low molecular weight ternary copolymer being within a range of 500 - 20,000.

2. An ionically cross-linked low molecular weight ternary copolymer as claimed in claim 1 wherein alkyl group of  
15 said alkyl acrylate or methacrylate has 1 - 4 carbon atoms.

3. An ionically cross-linked low molecular weight ternary copolymer as claimed in claim 1 wherein said low molecular weight ternary copolymer is obtained by thermally degrading ethylene-alkyl acrylate or methacrylate copolymer  
20 having a comparatively high molecular weight.

4. An ionically cross-linked low molecular weight ternary copolymer as claimed in claim 3 wherein said alkyl acrylate or methacrylate is ethyl acrylate or methacrylate.

5. An ionically cross-linked low molecular weight  
25 ternary copolymer as claimed in claim 3 wherein a melt index of said ethylene-alkyl acrylate or methacrylate copolymer having a comparatively high molecular weight is 300 g/10 min. or less,

and an alkyl acrylate or methacrylate content in the molecular chains is 0.5 to 25 mol%.

6. A process for producing an ionically cross-linked low molecular weight ternary copolymer which comprises reacting at least a part or the whole of acid groups in a low molecular weight ternary copolymer with a metallic cation selected from valences of 1 to 3, a content of ethylene being 80 - 99.5 mol% and a total content of acrylic or methacrylic acid and alkyl acrylate or methacrylate being 0.5 - 20 mol% in said low molecular weight ternary copolymer, a ratio of composition between said acid and said ester being 10 - 90 to 90 - 10%, and a viscosity-average molecular weight of said low molecular weight ternary copolymer being within a range of 500 - 20,000.

7. A process for producing an ionically cross-linked low molecular weight ternary copolymer as claimed in claim 6 wherein alkyl group of said alkyl acrylate or methacrylate has 1 - 4 carbon atoms.

8. A process for producing an ionically cross-linked low molecular weight ternary copolymer as claimed in claim 6 wherein said low molecular weight ternary copolymer is obtained by thermally degrading ethylene-alkyl acrylate or methacrylate copolymer having a comparatively high molecular weight.

9. A process for producing an ionically cross-linked low molecular weight ternary copolymer as claimed in claim 8 wherein said alkyl acrylate or methacrylate is ethyl acrylate or methacrylate.

10. A process for producing an ionically cross-linked low molecular weight ternary copolymer as claimed in claim 8 wherein a melt index of said ethylene-alkyl acrylate or methacrylate copolymer having a comparatively high molecular weight is 300  
5 g/10 min. or less, and an alkyl acrylate or methacrylate content in the molecular chains is 0.5 to 25 mol%.

11. A composition comprising:

(A) 100 parts by weight of at least one polymer selected from the group consisting of thermoplastic resins,  
10 thermosetting resins, rubber, and the mixture thereof; and

(B) 0.1 - 15 parts by weight of an ionically cross-linked low molecular weight ternary copolymer prepared by reacting at least a part or the whole of acid groups in a low molecular weight ternary copolymer with a metallic cation  
15 selected from valences of 1 to 3, a content of ethylene being 80 - 99.5 mol% and a total content of acrylic or methacrylic acid and alkyl acrylate or methacrylate being 0.5 - 20 mol% in said low molecular weight ternary copolymer, a ratio of composition between said acid and said ester being 10 - 90 to 90 - 10%, and  
20 a viscosity-average molecular weight of said low molecular weight ternary copolymer being within a range of 500 - 20,000.

12. A composition comprising:

(A) 100 parts by weight of at least one polymer selected from the group consisting of thermoplastic resins,  
25 thermosetting resins, rubber, and the mixture thereof;

(B) 0.1 - 150 parts by weight of a fine inert material;

and

(C) 0.1 - 20 parts by weight of an ionically cross-linked low molecular weight ternary copolymer prepared by reacting at least a part or the whole of acid groups in a low molecular weight ternary copolymer with a metallic cation selected from valences of 1 to 3, a content of ethylene being 80 - 99.5 mol% and a total content of acrylic or methacrylic acid and alkyl acrylate or methacrylate being 0.5 - 20 mol% in said low molecular weight ternary copolymer, a ratio of composition between said acid and said ester being 10 - 90 to 90 - 10%, and a viscosity-average molecular weight of said low molecular weight ternary copolymer being within a range of 500 - 20,000.